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HIGH PRESSURE COSMOCHEMISTRY APPLIED TO MAJOR PLANETARY INTERIORS: EXPERIMENTAL STUDIES

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SUMMARY

The overall goal of this project is to determine properties of the H-He-C-N-O system, as represented by small molecules composed of these elements, that are needed to constrain theoretical models of the interiors of the major planets. Much of our work now concerns the H_2O-NH_3 system. This project the first major effort to measure phase equilibria in binary fluid-solid systems in diamond anvil cells. Vibrational spectroscopy, direct visual observations, and x-ray crystallography of materials confined in externally heated cells are our primary experimental probes. We also are collaborating with the shockwave physics group at Lawrence Livermore Laboratory in studies of the equation of state of a "synthetic Uranus" fluid and molecular composition of this and other H-C-N-O materials under planetary conditions.

Detailed Description of Work in Progress During the Period 5/1/86-10/31/86

During the six-months covered by this report, our primary focus continued to be the NH_3-H_2O system in the composition range $(NH_3)_x(H_2O)_{1-x}$, $0 \leq x \leq 0.33$. Dr. Mary Johnson, a postdoctoral fellow formerly on this project and now at the California Institute of Technology, completed a manuscript that describes her visual observations of this system to 5 GPa from 240 to 370 K. This study provided a great amount of detailed information about this system at high pressures. However, she added two caveats: (1) Ice VI and ammonia dihydrate are difficult to nucleate from the liquid so it is not clear that equilibrium boundaries among these phases and the liquid have been established. (2) Solid phases can not be unambiguously identified by visual observations. This manuscript was submitted to the editors of the Journal of Geophysical Research in August; a preprint is appended to this report.

Our efforts during the Summer, therefore, emphasized two related activities: (1) trying to establish equilibrium among Ice VI, ammonium dihydrate, and liquid by approaching phase boundaries from several directions and (2) preparing samples of pure phases identified by Dr. Johnson and obtaining their x-ray diffraction patterns and vibrational spectra in order to augment visual methods of identification. Mr. Steven Boone continued the work on the phase boundaries by extending the visual studies system in the diamond-anvil high pressure cells, especially near 33% NH_3. Several samples were prepared and cycled repeatedly over a wide range of pressures and temperatures.

Although Mr. Boone's work is not complete, some samples were not reproducible after many cycles. Three likely sources of irreproduciblity are being examined: (a) reaction among ammonia, water, gaskets, and other components of the high pressure cell, (b) loss of material through cracks in the gasket, and (c) generation of new nucleation sites by cold working of the gasket which might change the rates at which equilibrium phases appear. Mr. Boone is attempting to determine the source of the irreproducibility by observing the effects of different gasket materials on the behavior of ammonia-water samples. With Mr. Cynn, he also is obtaining vibrational spectra of ostensibly pure phases so that the mixed-phase regions of the diagram can be characterized by spectroscopy.

Mr. Boone also is supervising construction of an autoclave for loading diamond anvil cells with mixtures of gases at moderate pressures. This apparatus will be used to prepare methane-water and ammonia-methane samples. The autoclave is being constructed from forged steels that are resistant to hydrogen embrittlement. Work on the autoclave was temporarily halted when internal cracks were discovered in the forging which is being replaced by the vendor.

Mr. Hyun-chee Cynn, a second-year student from the Graduate Geochemistry Program of the Department of Earth and Space Sciences, began to work on this project during the Summer. For his first task, Mr. Cynn prepared crystals of ammonia dihydrate in a Merrill-Bassett diamond-anvil cell with beryllium rockers that is especially suited for single-crystal x-ray diffraction work. The objectives of this task are to grow single crystals of ammonia dihydrate at room and low temperatures and to determine whether their structures are the same apart from small effects of thermal expansion and compressibility.

The first crystals were grown near room temperature from approximately 31-mole-percent aqueous NH_3 in 0.4-mm diameter holes in 0.2- to 0.4-mm thick Inconel X gaskets between diamonds with 0.8-mm culets. The ammonia dihydrate was identified by its known optical anisotropy under crossed polarizers. The pressure was determined to be about 10 kbar by the ruby luminescence method. For the initial x-ray study, the crystal was maintained at a pressure slightly higher than the melting pressure.

During September schedule, Mr. Cynn obtained use of the departmental Huber four-circle diffractometer for part of one week. This was the first time that he had used this diffractometer, and he managed to center the crystal and to scan the diffraction pattern for 38 hours. He identified seven strong independent reflections from 1811 that were sought. Preliminary analysis of the data suggest that ammonia dihydrate has a monoclinic-B structure. The observed lattice constants were: $a = 709.80$ pm, $b = 568.86$ pm, $c = 886.64$ pm, $\alpha = 90.008^{o}$, $\beta = 109.545^{o}$, and $\gamma = 90.401^{o}$. If the cell is monoclinic and contains four formulas, this would correspond to a not unreasonable density of 1.12 g cm^{-3}.

This first scan was terminated because the intensities of many expected reflections appeared to be very low. Observation of the sample at the end of the scan suggested, however, that the weak signals resulted from partial melting of the sample because of overnight temperature fluctuations in the x-ray laboratory and the proximity of the pressure and temperature of the sample to the melting line. Since then, Mr. Cynn has learned to grow single crystals of dihydrate at somewhat higher pressures and temperatures so that, after cooling to room temperature, they are further away from the melting line and less susceptible to temperature fluctuations. The diffraction patterns of such crystals at room and low temperatures will be obtained as soon as the diffractometer schedule permits. The techniques for growing single crystals of dihydrate also are being used by Mr. Cynn and Mr. Boone to prepare crystals for Raman and infrared spectroscopy.

During the period, two papers that described Dr. Johnson's contributions to studies of high pressure reactions and phase equilibria in the Fe and C-H systems appeared in print.

Bibliographic Data:

Publications Appearing or Submitted Between 5/1/86 and 10/31/86:

R. Boehler, M. Nicol, C.-S. Zha, and M.L. Johnson, "Resistance Heating of Fe and W in Diamond-Anvil Cells", Physica B **139/140** (1986) 916-918.

M.L. Johnson, M. Nicol, and N.C. Holmes, "Molecular Emission Spectra from Shock-Decomposed Benzene", in Y.M. Gupta, ed., **Shock Waves in Condensed Matter** (Plenum, New York, 1986), 201-206.

M.L. Johnson and M. Nicol, "The Ammonia - Water Phase Diagram and its Implications for Icy Satellites," (Submitted to J. Geophys. Res.)

Talks Related to Work Done on this Contract Presented Between 5/1/86 and 10/31/86.

Invited Poster: N.C. Holmes, M.L. Johnson, and M. Nicol, "Emission Spectroscopy of Shocked Benzene", Gordon Research Conference on Research at High Pressures, Meridan, June 1986.